Grain Growth Dependence on the Liquid Content in Liquid Phase Sintering

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Abstract

A model for grain growth during liquid-phase sintering is presented. A Rayleigh grain size distribution is assumed based on both experimental and theoretical results. This asymmetric distribution provides a continuous driving force for coarsening. The model uses the solid grain contiguity to calculate the relative solid-state and liquid-phase contributions to coarsening. The level of grain agglomeration affects both the mean diffusion distance and the interface area over which diffusion occurs. A cumulative grain growth rate is calculated assuming independent solid and liquid contributions to coarsening. Consequently, only the liquid volume fraction and the solid-liquid dihedral angle are required to predict the change in grain coarsening rate with solid-liquid ratio. A prior empirical correlation between the grain growth rate constant and the liquid volume fraction is compared to the resulting analytic form, showing excellent agreement. The new model is projected to be generically applicable to microstructure coarsening in multiple phase materials, including porous structures.

Liquid phase sintering (LPS) is a process for the densification of particulate materials such as tungsten carbide, silicon nitride, bronze, low alloy steels, stainless steels, tool steels, and various ceramics. The liquid provides a capillary force and the high transport rate that give rapid densification. However, the high diffusivity leads to progressive microstructural coarsening. Several authors have considered the problem of solid-liquid coarsening. Most of the models applied to liquid phase sintered structures are extrapolations of classic Ostwald ripening concepts developed for dilute solid contents. A dispersed grain structure allows the use of a mean field concept for calculation of the coarsening rate. This has some substantiation in that the grain size typically increases with the cube root of the isothermal hold time. However, the growth or contraction of a specific grain depends on the local environment, as established by various observations.

Semisolid systems, ranging from liquid phase sintering materials to metal-ceramic composites, evidence coarsening behavior very different from the assumptions in Ostwald ripening models. These materials have intertwined liquid and solid phases that coarsen at elevated temperatures. Consequently, there are many deficiencies with extending Ostwald ripening theories to semisolid alloys.

Liquid phase sintering is limited by Earth's gravity, because there are few systems where the solid and liquid densities are equal. Mechanical stability dictates multiple grain contacts to avoid collapse of the solid grain structure under the action of gravity. At these contacts, the grains form bonds. Once a steady-state is achieved, the bond size depends only on the grain size and the dihedral angle, while the number of bonds per grain depends largely on the liquid content. Net-shaping via LPS is most successful with less than 40 vol.% liquid and an intermediate dihedral angle (15° to 60°), giving sufficient rigidity to resist distortion. At high temperatures, the skeletal structure is not so strong that it inhibits densification. Consequently, the final microstructure consists of intertwined and connected solid and liquid networks. Grain agglomeration is a natural consequence of neck growth between contacting grains. Thus, dilute solid systems exhibit solid grain agglomeration when processed in microgravity or neutral buoyancy conditions.

Liquid phase sintering systems have varying dihedral angles (depending on the grain misorientations) and even nonspherical grain shapes. Except for a few cases the existing models do not allow for grain contact. They are only applicable to dilute solid suspensions without agglomeration, theoretically possible at low solid contents, probably below 20 vol.% solid. Most importantly, Ostwald ripening theories underestimate the grain growth rate constant for LPS systems. Another problem with extending Ostwald ripening to LPS involves systems that contain two solid phases. In these cases the reduced solid-liquid interface area gives slower growth. This has been traced to a change in contiguity or increase in dihedral angle. Several studies further show grain growth in LPS includes coalescence. Thus, the possibility of testing Ostwald ripening theories with LPS systems is fundamentally impeded by solid-solid grain contacts.

In spite of the difficulties in translating Ostwald ripening theory to grain growth in liquid phase sintering, one major success is evident. That is the general consensus that grain growth by diffusion through the liquid, termed solution-reprecipitation, follows a cubic law with an Arrhenius temperature dependence with an activation energy that correlates with diffusion through the liquid.

This model differs from the several theories of dilute solid content coarsening. The current model works in the LPS range, typically with less than 40 vol.% of second phase. Note that the Ostwald ripening models should not be extrapolated into the LPS range, and the LPS coarsening model should not be extrapolated into the Ostwald ripening range. The reasonable fit to available experimental LPS grain growth data is worthwhile. This behavior appears to be valid over the composition range typical to Earth-based liquid phase sintering with less than 40 vol.% liquid.

The conference research paper will show how grain growth during liquid-phase sintering has been understood through unique observations of microgravity and ground-based samples. The findings show a high level of grain agglomeration at all solid contents. This is an energetically favorable situation as compared to dispersed grains as typically treated in Ostwald ripening theory. The grain agglomeration affects the mean diffusion distance and the interface area over which diffusion occurs. Coarsening in liquid phase sintering depends on several factors that change with solid volume fraction. Critical findings from the microgravity experiments gives rules needed to fully model the coarsening process. An important observation is of a cumulative grain size distribution that follows the Rayleigh distribution. This distribution gives a growth rate calculation that brings both solid and liquid contributions into the overall grain growth rate. The assumption is that independent solid and liquid contributions lead to the overall observed rate of coarsening. Consequently, only the liquid volume fraction and solid-liquid dihedral angle are required to predict the change in grain coarsening rate with solid-liquid ratio. An empirical correlation between the grain growth rate constant and the liquid volume fraction to the inverse two-thirds power is compared to the new analytic form derived from the microgravity studies, showing excellent agreement.